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CONTAMINANTS IN COALS AND COAL RESIDUES

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1.0 INTRODUCTION

Coal is one of our most abundant sources of energy. Even with the enhanced role that coal will play in the future, known reserves are estimated to be sufficient for at least three or four centuries. The utilization of this form of fossil fuel, however, is fraught with environmental problems. In each step from mine to utilization various contaminants are released into the environment. The dust and gases in mines, drainage from coal mines and refuse, and stack emissions from coal-fired systems are examples of environmental problems that continue to plague our society.

In the past, the environmental degradation from coal mining, processing and burning was reluctantly accepted. However, concern over environmental quality has resulted in the establishment of regulations or guidelines for nearly all forms of coal utilization. Unfortunately, in many instances, the statutory regulation of coal pollution has preceded the availability of the technology necessary to achieve compliance with the law. Therefore, over the next decade, a massive effort must be launched to develop suitable environmental control technology. The technical approach to control of coal contamination, however, is not straightforward. Compromises and trade-offs between efficient energy use and the sometimes uncertain environmental consequences must be considered. Often the choice of control technology for one area will affect that required in another. Ultimately, decisions must be based on knowledge of the origins, magnitude and behavior of the various kinds of coal contaminants.

In this paper, we review some of the current information on the chemical and physical structure of coals to establish the source and nature of potential environmental contaminants. With this as background, we then discuss the nature of the major contaminants released into the environment during coal mining, handling, and combustion. Finally we will consider coal preparation, which is one of the most widely used forms of environmental control technology. Our discussion of coal cleaning will center on the environmental compromises and implications attendant in using this method to produce a cleaner burning fuel.

2.0 THE ORIGIN OF ENVIRONMENTAL CONTAMINANTS IN THE STRUCTURE OF COAL

Coal is a combustible carbonaceous rock formed from plant remains and various inorganic components (Fig. 1.3.1). Because of this, coal is a highly heterogeneous material that contains a wide variety of inorganic and organic impurities in addition to the carbonaceous matrix. Most of the environmental contamination from coals is a direct consequence of these impurities.

2.1 The Formation and Structure of Coal

The diverse composition of coal arises from the geological and chemical conditions present during coal formation. As outlined in Fig. 1.3.2, the first step

of coal formation is thought to be the deposition of plant remains and inorganic sediments under reductive conditions, usually in a freshwater swamp or lake. Eventually, under heat and pressure, these deposits are transformed into peat. The step from peat to coal is a chemical modification that involves mainly the loss of CO_2 and water.

Physically, coal contains both organic-rich and inorganic-rich regions. The organic part of the coal structure, which comprises about 70 to 90% of the total, is present in the form of distinct physical entities called macerals, which have differing sizes and shapes (Fig. 1.3.3). The morphologies of the macerals are thought to be related to the original plant constituents. The mineral matter in coals appears as small particles and grains or thick layers interspersed within the organic components.

2.2 Environmental Contaminants From the Organic Structure of Coal

The organic coal components contain mainly C, H, N, O and S; however, as detailed in Fig. 1.3.4, there is considerable variation in these elements in coals. Lower rank coals, such as lignite, are typified by a lower percentage of C and H and a relatively higher percentage of N, O and S, whereas the converse is true for the higher rank coals.

The organic matter in coals is predominantly in the form of aromatic and hydro-aromatic hydrocarbons. The O, S and N atoms form various functional groups that are dispersed throughout the carbon skeleton. The prevalent functional groups in coals are phenols, acids, ethers and groups containing sulfur and nitrogen.

Various models have been proposed to illustrate the structural details of the organic coal components. These are based on the known chemistry of coals, and are meant to suggest the major features of molecular composition rather than to be exact representations. One of the more popular structural models, devised by Wiser, is shown in Fig. 1.3.5. This structure, of course, bears a remarkable resemblance to the molecular configurations present in the humic components of plant materials.

The molecule pictured in Fig. 1.3.5 is very large, and, indeed, the general chemical inertness of coals is a reflection of the large sizes of their constituent molecules. However, during combustion, the large organic molecules can break down into smaller entities which can more easily escape into the environment as gaseous pollutants or as water contaminants. Also, coals contain some smaller organic molecules that are entrapped within the coal lattice. These may be released during processing or storage without the necessity of molecular cleavage.

By referring to the model in Fig. 1.3.5, it is relatively easy to envision the types of organic molecules that are released by coals during combustion, oxidation or weathering. Due to their preponderance, various aromatic and aliphatic hydrocarbons are common contaminants. Also, because heteroatom linkages are often susceptible to cleavage, molecules containing N, O and S atoms are prevalent coal contaminants. Typical examples of the types of organic molecules in the emissions or discharges from coals are pictured in Figs. 1.3.6a, b and c.

2.3 Environmental Pollutants From the Inorganic Constituents of Coal

Most of the inorganic coal components were deposited either as sediments in the original bed or as secondary materials during the formation of the coal; however, some of the trace or minor elements in coals were probably present originally in the plants.

The most abundant inorganic elements in coals (excluding S, N and O) are listed in Fig. 1.3.7. These are the elements that, for the most part, form the major minerals found in coals. These minerals fall into the four main classes listed in Fig. 1.3.8. They are the aluminosilicates (Na, K, Al, Si), the sulfides (Fe), the carbonates (Ca, Mg, Fe) and silica (Si). Generally, the aluminosilicates (clay minerals) and quartz tend to be chemically stable. Neither is volatile or likely to be leached from the coal. During combustion these minerals will form ash. Another troublesome aspect of the clay minerals is that they will fragment during burning to form small particulates (fly ash) that mix with the stack gases. The carbonates also form ash during combustion. In addition, they are partially water soluble and may be leached out of coals or wastes.

Among all of the coal constituents, environmental contamination caused by pyritic materials is the most severe. The sulfides are not particularly soluble or volatile *per se*, but when pyrite (or marcasite) is exposed to atmospheric conditions, it can interact with air and water at ambient temperature to produce soluble iron sulfate and sulfuric acid. This reaction of the iron sulfides in coals is, in fact, responsible for the formation of acid mine drainage, a most serious water pollution problem. Also, during the combustion of coal, the sulfur in the iron sulfides (along with added amounts of organic sulfur) is oxidized to SO_2 , the most prevalent air contaminant associated with the burning of coal. The chemical reactions for the formation of sulfuric acid and sulfur dioxides from iron sulfides appear in Fig. 1.3.9.

In addition to these major inorganic elements, coals also contain a wide variety of trace or minor elements. A listing of some of the trace elements of environmental concern in coals is given in Figs. 1.3.10a and b. The soluble forms of these elements may be released into the environment by aqueous leaching of coals or their residues. Also, some of the toxic trace elements assume volatile forms during coal burning; these can escape into the atmosphere along with the more inert gaseous products.

3.0 THE RELEASE OF ENVIRONMENTAL CONTAMINANTS FROM COALS DURING PROCESSING AND COMBUSTION

In the preceding section, we discussed the structure of coal, and how the various types of contaminants originate in the coal. In addition, we briefly considered how these contaminants are transported into the environment, either as gaseous or water-borne pollutants (Figs. 1.3.11a and b). In this section, we will consider the types of contaminants that are released from coals during the various processing and utilization steps. Then, we will go on to discuss the environmental circumstances surrounding coal preparation, particularly to emphasize its use as an environmental control method.

The usual sequence of coal production and utilization steps appears in Fig. 1.3.12a. After mining, nearly all coal is subjected to storage and transportation steps prior to utilization (combustion). In addition, about one-half of the coal mined in the U.S. is washed or prepared before it is used to remove some of the unwanted mineral matter. Each processing, handling or utilization step results in the production of significant environmental pollutants.

3.1 Environmental Pollution from Coal Mining

Coal mining is one of our most dangerous industries. Therefore, the environmental and health hazards associated with this phase of coal production are under much scrutiny. As shown in Fig. 1.3.12b, both atmospheric and aqueous contaminants are produced by coal mining.

The main atmospheric contaminants from coal mining are dust and gases. Dust is generated by physical abrasion of the coal, and under confined conditions, such as in underground mines, the respiration of this dust is a major health problem. The release of methane and other combustible gases from the coal beds is another serious problem associated with coal mining. Underground, when ventilation is poor, these gases can accumulate in explosive concentrations.

Acid drainage is by far the most serious water problem associated with coal mining. As detailed earlier, acid formation results from the pyritic material present in the coal. More than 3-million tons of sulfuric acid are discharged annually into waterways from coal mines. Acid mine drainage is responsible for contaminating some 7,000 miles of streams in the Appalachia region.

The spoil material from coal mining (overburden and mine wastes) contributes to contamination on a much smaller scale than do mines. For environmental purposes most of this type of waste is used as fill material after mining has been completed. However, coal mine spoils are a local source of acid drainage and mineral contaminants in water.

3.2 Contaminants Produced by Coal Storage and Transportation

Neither the seriousness nor the extent of environmental contamination from coal storage or transportation has been adequately assessed. As seen in Fig. 1.3.12c, the potential exists for the release of pollutants into both the atmosphere and aqueous environment during these handling operations. Because of the transient nature of coal during storage and transportation, gaseous and aqueous pollutants from these sources will often be more diffuse or less visible than those from stationary sources.

3.3 Environmental Contamination From Coal Combustion

The environmental contaminants produced by the burning of coal in boilers, power generators and other stationary sources (see Fig. 1.3.12d) are well identified, and we need dwell only briefly on this topic here.

The oxides of sulfur, nitrogen and carbon are the most notorious air contaminants produced by the combustion of coal. These contaminants enter the atmosphere in great quantities. In 1974, about 20-million tons of SO_2 and 5-million tons of

nitrogen oxides (NO_x) were discharged into the environment from coal burning. In addition to these gaseous contaminants, coal combustion also produces large quantities of finely divided mineral particulates (fly ash) that also escape into the environment in copious quantities. Finally, in the last few years it has been recognized that certain toxic trace elements, such as Pb, Hg, As and Cd may be released into the atmosphere in worrisome quantities from coal combustion sources. It is not yet clear whether these elements are in a completely volatile state or whether they are adsorbed at the surface of fly ash or other particulate emissions.

The burning of coal also produces solid waste materials that need to be disposed of in environmentally compatible ways. The bulk of this residue is bottom ash formed by the nonvolatile mineral matter in the coal. In addition, to lessen the air pollution load, increasing amounts of fly ash are being removed from the stack components by precipitators and other devices. About 70-million tons of bottom and fly ash are produced annually in the U.S. from coal combustion. There is growing awareness that the discarded solid wastes from coal combustion may themselves be a serious source of environmental contamination. In particular, these materials may be subjected to leaching by rainwater or surface flows that could produce mineral or trace element contamination.

3.4 Environmental Contaminants From Coal Preparation

The final coal processing step that we will consider is coal washing or preparation. In contrast to the previous areas discussed, this step is conducted specifically to reduce the concentration of some of the undesirable mineral impurities. There are, of course, economic benefits to be derived from coal washing, such as the reduced cost of shipping, storing and burning a higher quality product, but for the future, coal preparation is best envisioned as a pollution control measure.

Coal preparation is largely a mechanical process, involving a series of crushing, sizing, separating and drying steps. In most cases, the coal is separated from the mineral matter on the basis of density. Modern coal preparation plants can recover about 90% of the energy content of the coal, while reducing the sulfur content to less than 1%.

The mineral refuse and wastes from coal preparation are also a recognized source of environmental contamination, as detailed in Figs. 1.3.12e and 1.3.13. Coal preparation refuse is subjected to weathering and leaching processes that frequently produce acids and highly mineralized drainage. The relative seriousness of this problem can be judged by comparing the quality of the aqueous effluents from typical coal refuse dumps (Fig. 1.3.14) with the proposed EPA standards for such effluents shown in Fig. 1.3.15. It is seen that in no instance does the quality of the waste bank effluents (e.g., see the Fe, Al, Mn and pH values) approach the criteria established by EPA. It has been estimated that more than 3000 miles of streams in Appalachia alone are contaminated from coal refuse dumps.

In addition to water contamination, burning refuse dumps produce substantial air pollution. Approximately 1% of the total nationwide quantities of sulfur-, nitrogen- and carbon-oxide emissions are attributed to burning coal wastes.

Although this may be considered a small contribution, these contaminants occur in highly localized regions. Finally, we must also point out that structural instabilities in coal refuse banks have resulted in landslides or cave-ins that have claimed several hundred lives over the last 20 years. The problems associated with coal refuse dumps are not isolated incidences. Of the 3000 to 5000 refuse dumps in the U.S., about one-half are the source of some type of health or environmental problem.

3.5 Environmental Trade-offs in the Coal Preparation/Utilization Cycle

A primary function of coal preparation is to reduce the mineral matter in raw coals so that the emissions from the burning of these coals can meet established guidelines. Indeed, about 100-million tons of potential contaminants are removed annually from U.S. coals by coal preparation. The waste materials produced by coal preparation are a major source of environmental contamination.

As shown in Figs. 1.3.16 and 1.3.12f, coal preparation is in effect an environmental trade-off: a serious health and pollution problem is simply being transferred from one segment of the environment to another. Undoubtedly the rationale for this transfer is based on the assumption that contamination from solid waste materials concentrated in remote disposal areas is easier to control or alleviate than the more ubiquitous forms that are discharged by the burning of coal. Conceivably, the combined hazards from coal refuse dumps present a less serious threat to human health than the highly mobile emissions from burning coal, although this point could be debated at some length. Environmental control of discarded coal refuse, until recently, has been largely neglected. Until adequate assessment and cleanup of this source of contamination is effected, the full implications of coal preparation as a viable pollution control measure cannot completely be evaluated.

4.0 SUMMARY

Most of the major environmental pollutants from coals originate as impurities in the coal structure. These include various organic compounds, minerals and trace elements that are released into the air and water when coal is mined, processed, and utilized. The use of coal preparation to produce cleaner burning fuels involves an environmental compromise, wherein reduced emissions and solid wastes from coal burning sources are achieved at the expense of greater environmental degradation from coal cleaning wastes.

5.0 GENERAL REFERENCES

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• Fig 1.3.1

WHAT IS COAL ?

COAL IS A COMBUSTIBLE SEDIMENTARY ROCK
FORMED FROM PLANT MATERIALS AND
INORGANIC SEDIMENTS IN VARIOUS STAGES
OF METAMORPHISM

Fig. 1.3.2

COAL-FORMING PROCESSES

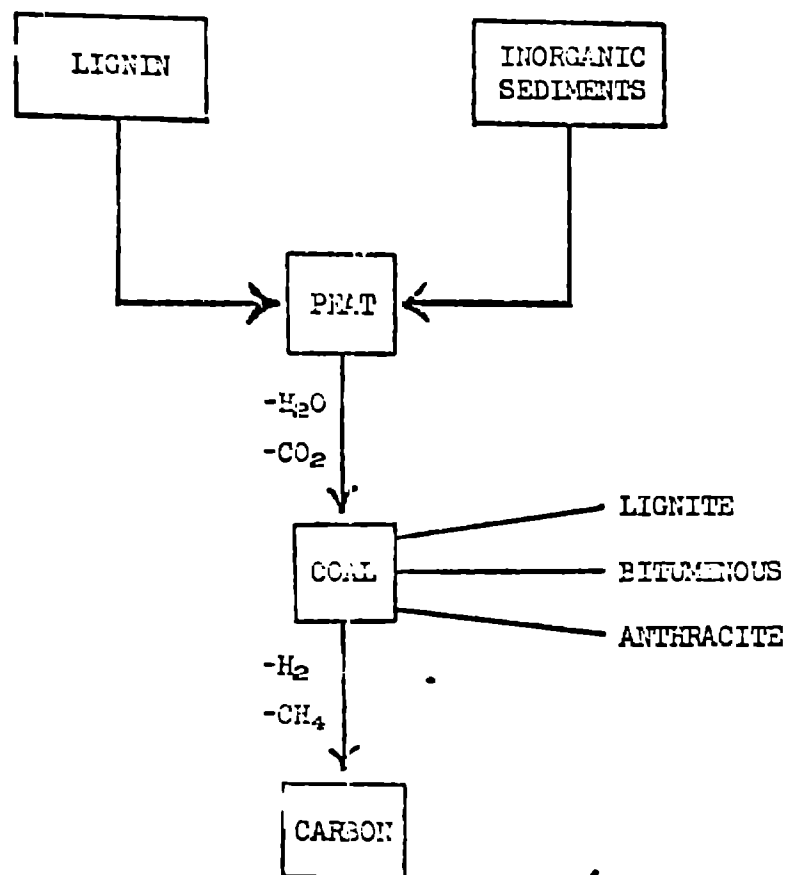


Fig. 1.3.3

PHYSICAL COMPOSITION OF COAL (SPACKMAN)

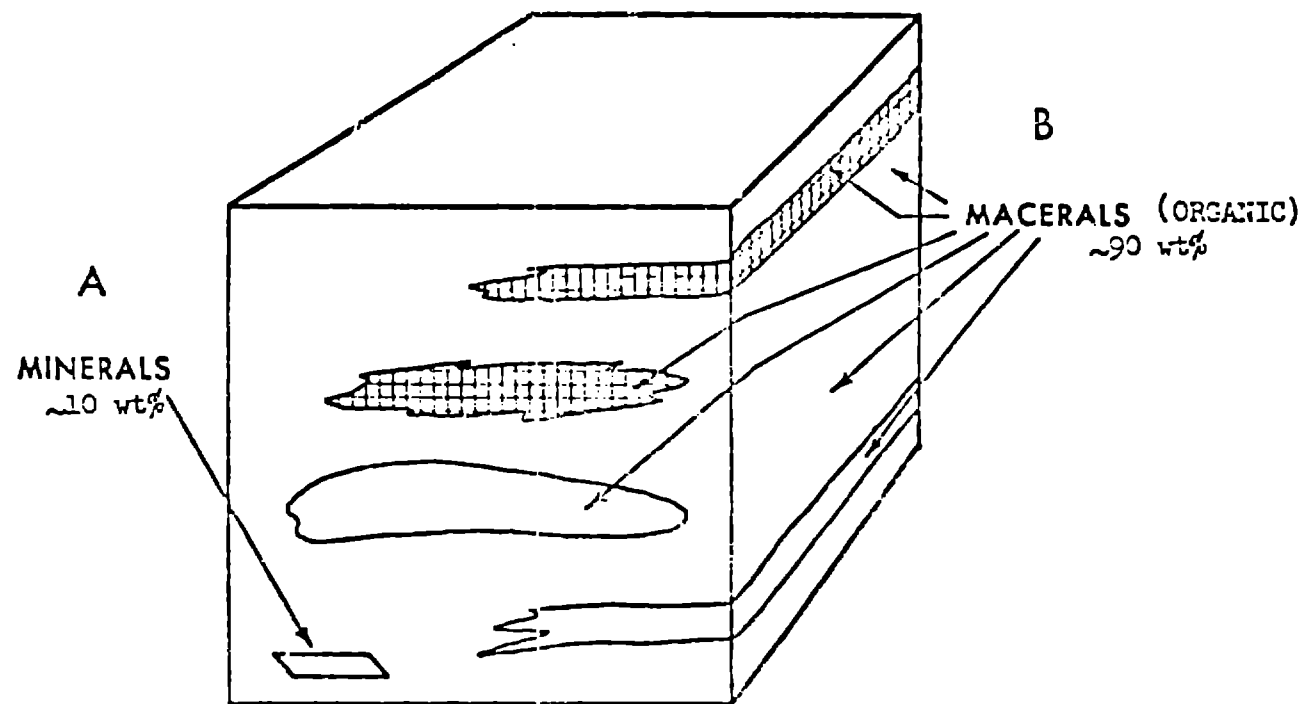
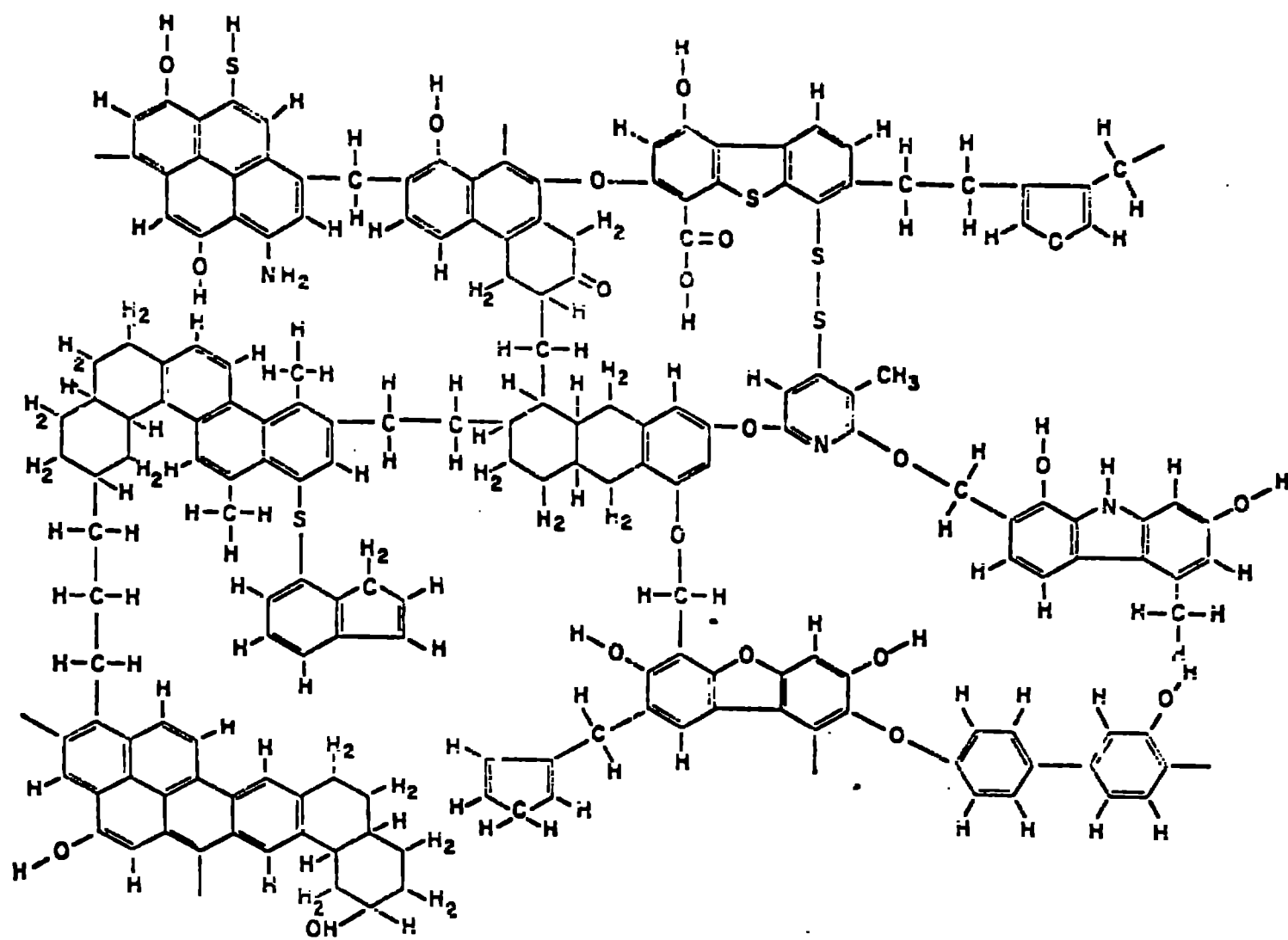


Fig 1.3.4

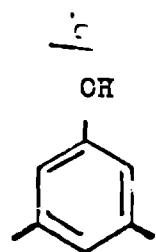
ELEMENTAL COMPOSITION OF ORGANIC COAL COMPONENTS

<u>ELEMENT</u>	<u>RANGE (WT %)</u>
CARBON	65 - 93
HYDROGEN	2.0 - 6.0
OXYGEN	2.0 - 20
SULFUR	0.5 - 5.0
NITROGEN	0.5 - 2.0

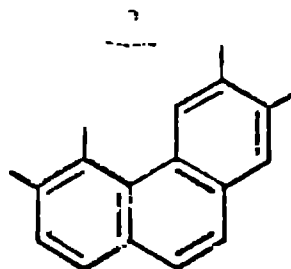
FUNCTIONAL GROUP MODEL OF BITUMINOUS COAL (WISER)



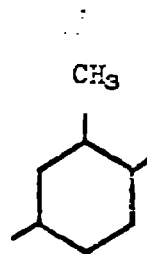
1, 3, 6 a, b and c
POTENTIAL ORGANIC CONTAMINANTS FROM COALS



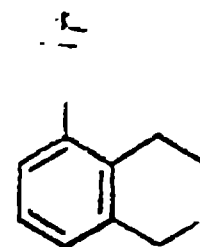
PHENOLS



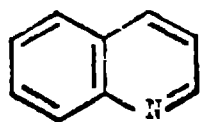
AROMATIC HYDROCARBONS



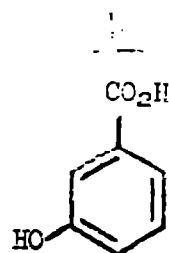
ALICYCLIC HYDROCARBONS



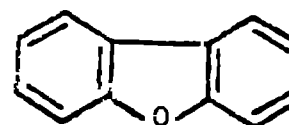
POLYCYCLIC HYDROCARBONS



NITROGEN HETEROCYCLICS



ACIDS



OXYGEN HETEROCYCLICS

MAJOR INORGANIC ELEMENTS IN COALS

<u>ELEMENT</u>	<u>RANGE (wt%)</u>
Na	0 - 0.2
Mg	0.1 - 0.3
Al	0.4 - 3.1
Si	0.6 - 6.1
K	0.1 - 0.4
Ca	0.1 - 2.7
Ti	0.0 - 0.3
Fe	0.3 - 4.3

Fig. 1.3.2
MAJOR MINERALS IN COALS

ALUMINOSILICATES (10-90 wt%)

ILLITE

KAOLINITE

MIXED LAYER CLAYS

CARBONATES (0-10 wt%)

CALCITE

DOLOMITE

SIDERITE

SULFIDES (0-40 wt%)

PYRITE

MARCASITE

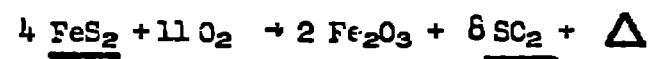
. SILICA (0-20 wt%)

QUARTZ

Fig 15.1

IRON SULFIDES CAUSE MAJOR ENVIRONMENTAL PROBLEMS

SULFUR OXIDE EMISSIONS



ACID MINE DRAINAGE



TRACE ELEMENTS OF ENVIRONMENTAL CONCERN IN COAL

<u>ELEMENT</u>	<u>RANGE (ppm)</u>
Be	0 - 31
Mn	6 - 181
Ni	0.4 - 104
Cu	2 - 185
Zn	0 - 6000
As	0.5 - 106
Se	0.4 - 8
Y	0.1 - 59
Cd	0.1 - 65
Hg	.01 - 1.6
Pb	4 - 218

SUMMARY OF POTENTIAL ENVIRONMENTAL CONTAMINANTS IN COALS

AQUATIC TRANSPORT MODE

a

- SOLUBLE ORGANIC MOLECULES
 - POLYAROMATIC HYDROCARBONS
 - LEACHABLE MINERALS AND TRACE ELEMENTS
 - ACID DRAINAGE
-

ATMOSPHERIC TRANSPORT MODE

b

- VOLATILE HYDROCARBONS .
- PARTICULATES AND DUST
- VOLATILE TRACE ELEMENTS
- OXIDES OF SULFUR, NITROGEN AND CARBON

Fig. 1.3.12 a - F

Environmental Contaminants from
Coal Processing and Utilization

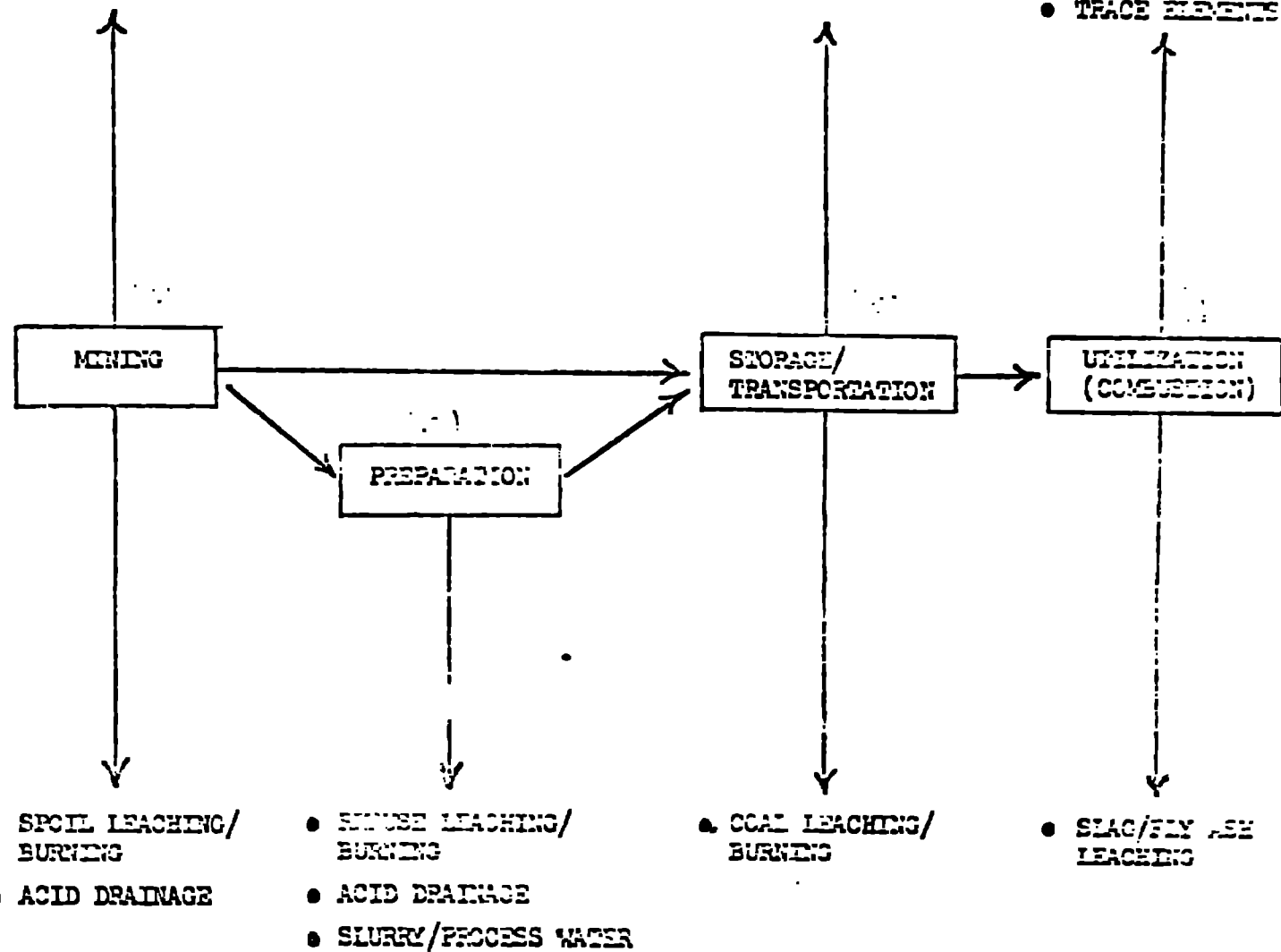
ATMOSPHERIC
POLLUTION

- HYDROCARBON GASES
- DUST

- HYDROCARBON GASES
- DUST

- SULFUR, NITROGEN AND CARBON OXIDES
- PARTICULATES
- TRACE ELEMENTS

COAL
PROCESS (a)
STEP



AQUATIC/
TERRESTRIAL
POLLUTION

- SPOIL LEACHING/
BURNING
- ACID DRAINAGE

- SPOIL LEACHING/
BURNING
- ACID DRAINAGE
- SLURRY/PROCESS WATER

- COAL LEACHING/
BURNING

- SLAG/FLY ASH
LEACHING

(5) Utilization

Fig 1.3.13

ENVIRONMENTAL PROBLEMS
FROM DISCARDED COAL WASTES

- STRUCTURAL INSTABILITIES
- ACIDIC AND MINERALIZED DRAINAGE
- WASTE DUMP BURNING

Fig 1.3.14

DRAINAGE FROM PENNSYLVANIA COAL REFUSE DUMPS

<u>Sample</u>	<u>pH</u>	<u>Conduct</u>	<u>SO₄</u>	<u>Fe</u>	<u>Al</u>	<u>Mn</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>
1	3.1	13600	40500	6168	999	63				
2	2.7	12400	17750	3197	1014	31				
3	3.7	3500	1125	130	69	15				
4	3.0	4400	3000	30	87	50	340	250	100	5
5	4.0	3000	1600	1	50	90	180	140	60	15

Concentrations in ppm

Conductance in micromhos-cm²

Fig. 1.3.15

EPA PROPOSED REGULATIONS FOR AQUEOUS EFFLUENTS FROM
COAL MINING POINT SOURCES - OCTOBER 1975

Effluent characteristic	Maximum for any 1 day (milligrams per liter)	Average of daily values for 30 consecutive days shall not exceed (milligrams per liter)
Iron, total	7.0	3.5
Iron, dissolved	0.60	0.30
Aluminum, total	4.0	2.0
Manganese, total	4.0	2.0
Nickel, total	0.40	0.20
Zinc, total	0.40	0.20
TSS	70	35
pH	Within the range 6.0 to 9.0	

Fig 1.3.1's

ENVIRONMENTAL TRADE-OFFS FOR COAL PREPARATION

- REDUCED ATMOSPHERIC EMISSIONS FROM COAL COMBUSTION
- REDUCED SOLID WASTES FROM COAL COMBUSTION

VERSUS

- INCREASED SOLID AND LIQUID WASTES FROM COAL PREPARATION